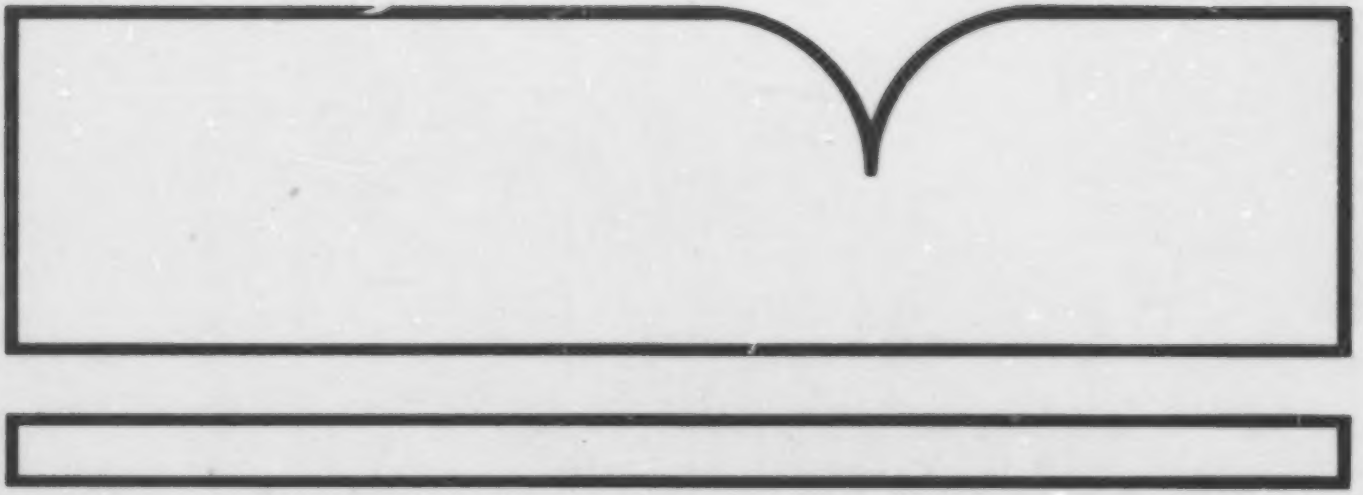
PB82-127317

A Comprehensive Scheme for Multimedia Environmental Assessment of Emerging Energy Technologies

(U.S.) Industrial Environmental Research Lab.
Research Triangle Park, NC

Oct 81



U.S. Department of Commerce
National Technical Information Service
NTIS.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1.	2.	3. RE
EPA-600/J-81-353	Journal Article	PB82-127317

4. TITLE AND SUBTITLE	5. REPORT DATE
A Comprehensive Scheme For Multimedia Environmental Assessment of Emerging Energy Technologies	1981 October 1981
	6. PERFORMING ORGANIZATION CODE 4 316009
7. AUTHOR(S) Frank E. Briden, James A. Dorsey and Larry D. Johnson (EPA/IERL-RTP)	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS see block 12	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS **EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711**	13. TYPE OF REPORT AND PERIOD COVERED Journal Article, 1981
	14. SPONSORING AGENCY CODE **EPA/600/13**

15. SUPPLEMENTARY NOTES Published in International Journal of Environmental Analytical Chemistry, Vol. 9, pp. 189-208, 1981.

16. ABSTRACT

The paper discusses new requirements imposed by the emergence of technologies (being developed to meet world energy needs) on existing environmental analytical capabilities. A three-phase, multimedia, environmental assessment scheme has been designed and implemented which characterizes the chemical and biological impact of process streams. Level 1 is a screening phase which emphasizes completeness of detection of elements, classes of organic materials, and acute biological responses. Level 2 seeks to identify specific substances identified in Level 1 as potential environmental problems and confirm the biological response. Level 3 is a quantitative study of the effect of process variables on the emission rate of specific substances indicated in Level 2. To demonstrate the effectiveness of Level 1, the quantitative and semi-quantitative organic results are derived from experimental data. The Level 1 results are then compared with the Level 2 technique of gas-chromatography/mass-spectroscopy. For this data it was seen that Level 1 is very efficient for the detection of pollutants while broad enough to cover a complete source characterization.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Assessments	Stationary Sources	14B
Energy	Environmental Assessment	14G
Energy Conversion Techniques		10A
Industrial Processes		21B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	**Unclassified**	
	20. SECURITY CLASS *(This page)* **Unclassified**	22. PRICE

EPA Form 2220-1 (9-73)

PRODUCT OF:
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/J-81-353
Journal Article

Intern. J. Environ. Anal. Chem., 1981, Vol. 9, pp. 189–208
0306-7319/81/0903-0189 $06.50/0
© Gordon and Breach Science Publishers Inc., 1981
Printed in Great Britain

A Comprehensive Scheme for Multimedia Environmental Assessment of Emerging Energy Technologies†

FRANK BRIDEN, JAMES DORSEY and LARRY JOHNSON

Process Measurements Branch, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

(*Received July 9, 1980*)

The emergence of technologies being developed to meet world energy needs imposes new requirements on existing environmental analytical capabilities. These emerging technologies present unknown challenges to the environment and it is important to develop analytical schemes capable of comprehensively characterizing potential environmental problems.

We have designed and implemented a three-phase, multi-media, environmental assessment scheme which characterizes the chemical and biological impact of process streams. Level 1 is a screening phase which emphasizes completeness of detection of elements, classes of organic materials, and acute biological responses. Level 2 seeks to identify specific substances identified in Level 1 as potential environmental problems and confirm the biological response. Level 3 is a quantitative study of the effect of process variables on the emission rate of specific substances indicated in Level 2.

Level 1 is a standardized procedure utilizing broad capability detection techniques such as spark-source mass spectrometry, ion-chromatography, liquid-chromatography, infra-red spectrophotometry and low resolution mass spectrometry. Biological techniques include cellular, bacterial and whole animal acute toxicity tests.

Level 2 techniques are chosen from a battery of recommended procedures on a sample-specific basis. Included among Level 2 techniques are atomic-absorption, X-ray diffraction and gas-chromatography-mass spectrometry.

To demonstrate the effectiveness of Level 1, the quantitative and semi-quantitative organic results are derived from experimental data. The Level 1 results are then compared with the Level 2 technique of GCMS. For this data it was seen that Level 1 is very efficient for the detection of pollutants while broad enough to cover a complete source characterization.

KEY WORDS: Environmental assessment, energy, multimedia, low resolution mass spectrometry, gas-chromatography mass spectrometry.

---

†Paper presented at the 10th Annual Symposium on the Analytical Chemistry of Pollutants, May 1980, Dortmund, GFR.

INTRODUCTION

The Process Measurements Branch (PMB) provides analytical support for EPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina (IERL-RTP). A major function of PMB is to design and troubleshoot techniques for the evaluation of various industrial pollution control methodologies. Pollution control assessment can cover the entire spectrum of industrial and energy production activities as shown in Figure 1. In the early days of its existence, PMB learned that quite often the analytical data needed from a source evaluation was greater than previously estimated. Early studies also revealed that when a source evaluation was performed the data acquired did not provide a comprehensive characterization of materials released into the environment. It was further recognized that a standard assessment scheme would greatly enhance data comparison studies of different sources.

In a move to increase the quality and usefulness of the data acquired, PMB developed a phased approach for IERL-RTP's Environmental Assessment Program. The basic components of the Environmental Assessment Program are: (1) a systematic evaluation of the physical, chemical and biological characteristics of the streams associated with a process; (2) predictions of the probable effects of the streams on the environment; (3) the prioritization of the streams; and (4) identification of any necessary control technology programs.

The phased approach for the Environmental Assessment Program provides three levels of sampling and analysis. Level 1 indicates if a potentially hazardous concentration is present in the source that has been tested. It indicates element levels for inorganics, and for organics yields the compound class and, in some cases, the specific compounds. It provides information on the *in-vitro* cytotoxicity and mutagenicity of the source as well as acute aquatic effects. Level 2 provides more quantitative compound identification for any hazardous species found by Level 1. Level 2 can also be activated by biological testing should Level 1 chemical methods miss a particular synergistic combination. At the culmination of Level 2, all hazardous compounds should be identified. Level 3 is a long-term monitoring phase. It is initiated to determine variations of the hazardous materials in an industrial stream with time to evaluate the efficiency of control strategies. This phased approach offers potential benefits in terms of: the quality of information that is obtained for a given level of effort and the costs per unit of information. Investigations and comparisons of the phased approach with more traditional approaches have revealed substantial savings in both time and funds required for assessments.

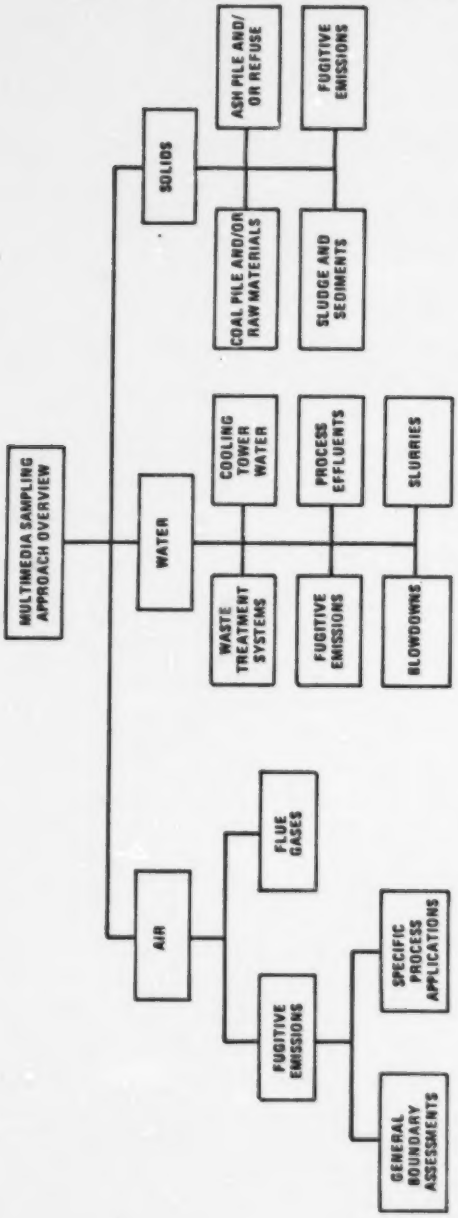


FIGURE 1 Multimedia sampling strategy overview.

The phased approach has been successfully implemented on a number of projects with the approach improved as experience has been gained. Level 1 was the first phase implemented; therefore, it has been subjected to considerable scrutiny and improvement. Data from Level 2 studies are just becoming available and only recently have comparisons of these two data levels been possible. This discussion, therefore, will provide insight on the resolution of the more general Level 1 data and the more specific Level 2 data.

Level 1 is a complete survey of all streams for a process. The sampling and analytical procedures are rigorously defined for gases, liquids and solids. For each sample, there is an analytical scheme which covers the physical, chemical and biological characterization of the sample. As a result of Level 1 analysis, it will be possible to determine if any process streams represent a potential hazard to the environment. The physical properties are obtained by the sizing of particulate material with cyclones and optical microscopy. The elemental composition is determined with spark source mass spectrometry for 73 elements and atomic absorption for mercury. Bulk solids are analyzed for fluoride, chloride, nitrite, nitrate, sulfite, sulfate, and phosphate ions by ion chromatography, after extraction.

The organic composition is derived through a procedure which utilizes liquid chromatography, infrared spectrophotometry, low resolution mass spectromerty, gravimetry, and total chromatographable organic determinations.

Since biological effects can't be predicted solely from physical and chemical data, it has been necessary to include biological tests in the environmental assessment. The Level 1 screening phase uses a series of short-term bioassays for the detection of acute biological effects. The bioassays can be divided into health-related tests and ecological tests. The health tests were selected to screen for both acute toxic and potential chronic (i.e., carcinogenic) health effects. The rodent acute toxicity test employs a quantal prescreen in rats followed by a quantitative assay. The cellular toxicity assay in mammalian cells measures cellular viability or survival as well as more sensitive metabolic endpoints. The cells employed in Level 1 are rabbit alveolar macrophage (RAM) for particulates, and Chinese Hamster Ovarian (CHO) for liquids. Also included in the health tests is the Ames *Salmonella typhimurium* reverse mutation assay. This assay uses bacteria to screen complex process samples for potential mutagenic or carcinogenic activity.

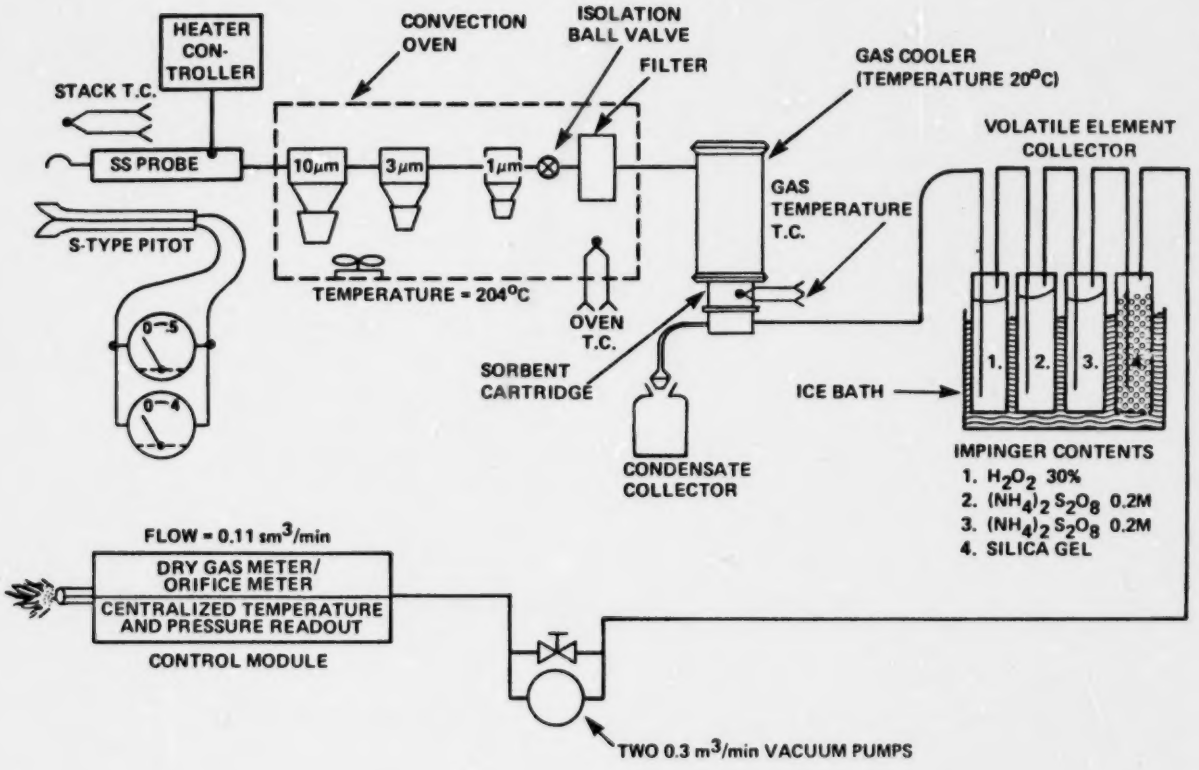
The aquatic ecological tests measure acute toxic effects of an industrial effluent or emission on freshwater or marine fish (fathead or sheephead minnows), freshwater or marine invertebrates (Daphnia or grass shrimp),

and selected species of freshwater or marine algae. The aquatic ecological tests are "static" tests, involving the exposure of the various organisms to several concentrations of an effluent sample in a closed system or aquarium. The organisms are monitored for abnormal responses or death.

Terrestrial ecological tests, including root elongation, plant stress ethylene, and insect tests, are under evaluation; these tests are being developed and will be part of the Level 1 protocol in the near future. The root elongation test evaluates samples via the inhibitory effect of toxic chemicals on seed germination and root elongation. The plant stress ethylene test assays samples by way of the release of ethylene by plants when the plants are exposed to toxic gases. The insect test will measure the toxicity of solid, liquid, or gaseous samples on sensitive insect species.

One of the major contributions to environmental pollution is the flue gas coming from energy-producing processes. Since this process stream is so complex, it has presented a major challenge to environmental assessment. It is comprised of: fixed gases from the atmosphere and the combustion process, sulfur containing gases from the fuel breakdown, organic and reduced gases from incomplete combustion, organic vapors, organic and inorganic particulate, and volatile elements.

In order to obtain a complete assessment of particulate-laden, flue gas streams, the source assessment sampling system (SASS) was designed by the Process Measurements Branch. The schematic layout is seen in Figure 2. The sample from the stack is taken within a specified tolerance of isokinetic conditions at a point previously determined to be at the average stack velocity. The sample enters the SASS train via a stainless steel probe that is directly attached to an oven which, like the probe, is maintained at 204°C. Within the oven are three particle collecting cyclones and a filter. The cyclones have cut-points of 10, 3 and 1 μm, respectively. The remainder of the particulate is trapped on the filter. The sample upon leaving the oven enters the gas cooler which cools the gas stream to 20°C. The cooled gas then enters the organic sorbent trap which contains XAD-2 resin. This resin has been chosen as a result of considerable work done to evaluate the available resins.[1] The condensation solution from the gas cooler and the sorbent trap falls into the condensate collector. The gas stream then enters a series of four impingers. The first impinger employs hydrogen peroxide to oxidize reducing gases such as sulfur dioxide which could deplete the oxidation capacity of the following impingers. The next two impingers are used to collect the volatile elements—mercury, arsenic, and antimony—by oxidizing them to soluble ions. The last element of the train is an impinger vessel filled with silica gel to collect moisture which is harmful to the vacuum pumps. The gas flow is measured with a dry gas meter or an orifice meter. All of the liquid and solid samples from the


HEATER CON-TROLLER
STACK T.C.
SS PROBE
S-TYPE PITOT
0—5
0—4
CONVECTION OVEN
10μm
3μm
1μm
TEMPERATURE = 204°C
ISOLATION BALL VALVE
FILTER
OVEN T.C.
SORBENT CARTRIDGE
CONDENSATE COLLECTOR
GAS COOLER (TEMPERATURE 20°C)
GAS TEMPERATURE T.C.
VOLATILE ELEMENT COLLECTOR
ICE BATH
1.
2.
3.
4.
IMPINGER CONTENTS
1. H_2O_2 30%
2. $(NH_4)_2 S_2O_8$ 0.2M
3. $(NH_4)_2 S_2O_8$ 0.2M
4. SILICA GEL
FLOW = 0.11 sm^3/min
DRY GAS METER/ ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
TWO 0.3 m^3/min VACUUM PUMPS

SASS train are removed, packed, and shipped to the analytical laboratory according to schemes which are designed to prevent or minimize sample loss or degradation. The sample volume needed to determine hazardous pollutants at the level at which they become hazardous is 30 dry standard cubic meters (dsm^3). The SASS train has been designed to operate at about 0.11 dsm^3 flow rate so the 30 dsm^3 sample can be collected in about 4.5 hours. The flow rate should be maintained within -30 to $+50$ percent of the isokinetic rate. The SASS train requires 60 amps at 110 volts electrical power to operate all components. The SASS train samples are analyzed in the laboratory.

The gases and volatile organic compounds (bp $< 100°C$) must be analyzed in the field. They are taken from the source with an integrated gas sampling train which consists of a gas-cooling condenser, a polymer sandwiched aluminium bag which is expanded within a rigid container by means of a diaphragm type, or equivalent, pump. The fixed gases (CO, CO_2, N_2, O_2) are then determined by gas chromatography (GC) with a helium carrier gas molecular sieve column and a thermal conductivity detector. The sulfur-containing gases H_2S, SO_2 and COS are determined by GC using a flame photometric detector or a thermal conductivity detector if sulfur-containing gases are present in large amounts. Ammonia, hydrogen cyanide, and cyanogen are determined by GC with a thermal conductivity detector. The nitrogen oxides are determined by EPA Method 7 or by an in-line chemiluminescence NO_x analyser. With Method 7, the oxides convert to nitrate which reacts with phenol-disulfonic acid to yield 6-nitro-2, 4-phenoldisulfonic acid and colorimeteric measurement of the product. The volatile organics are determined by GC with a flame ionization detector.

ANALYSIS OF SASS TRAIN SAMPLES

Figure 3 shows a block diagram of the SASS train components and the disposition of the samples it produces. The particulate from the first two cyclones (particulate $> 3\,\mu m$) are combined and analyzed by spark source mass spectrometry for 73 elements and by atomic absorption for mercury. The particulate is also extracted with methylene chloride in a Soxhlet extractor and the extract subject to organic analysis consisting of gravimetry, gas chromatography, infrared spectrophotometry, liquid chromatography and low resolution mass spectrometry. A portion of the particulate is subjected to bioassay procedures which were discussed earlier. The particulate from the third cyclone and the filter (particulate $< 3\,\mu m$) are combined and treated exactly like the previous sample.

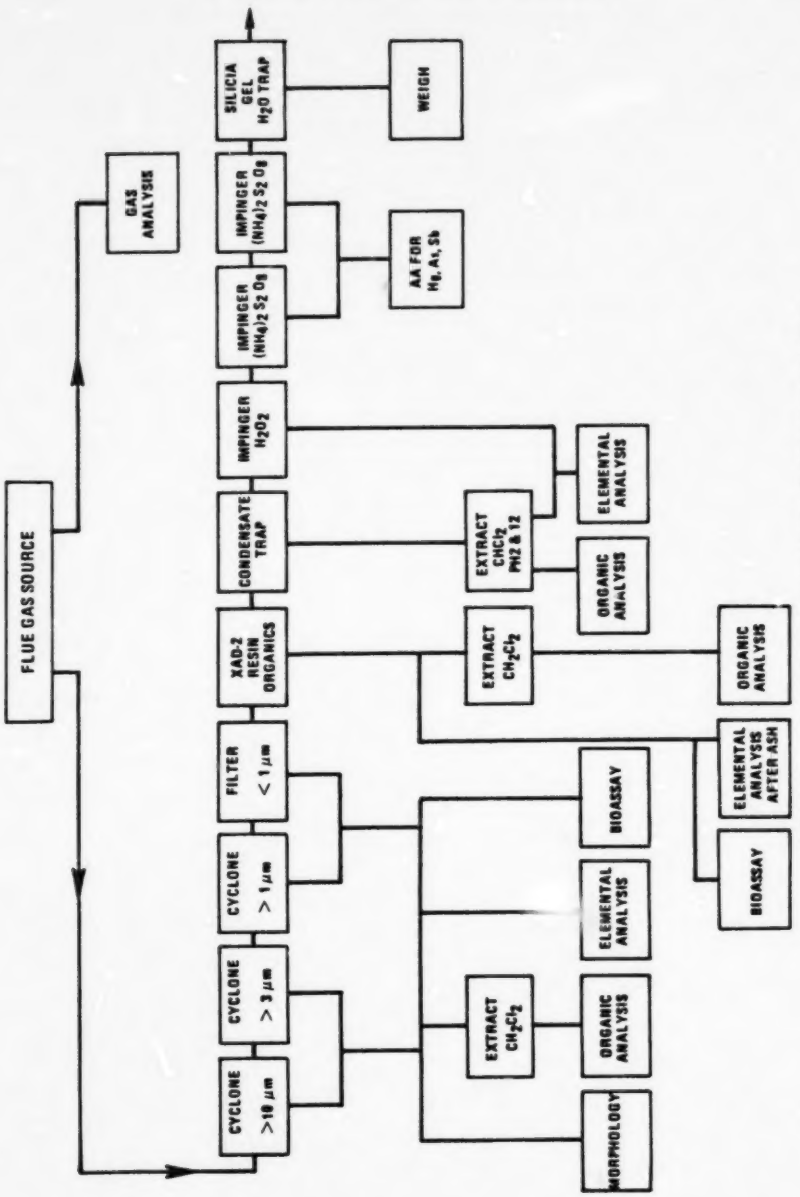


FIGURE 3 Sample disposition for level 1 SASS analysis of flu gas.

ELEMENTAL ANALYSIS

In performing Level 1 elemental analysis, spark source mass spectrometry (SSMS) has been designated for 73 elements with atomic absorption recommended for mercury. Although other multi-element analytical methods may give more accurate or sensitive results for particular elements, it has been determined that SSMS yields adequate accuracy for more elements at a lower cost per element than any other multi-element technique. With SSMS, elements can be determined with minimal matrix effects. Also, it is very significant that SSMS circumvents the complex problems of sample dissolution, and provides results within two working days from sample submission. Since mercury is not determined satisfactorily by SSMS, it is necessary to determine it by atomic absorption (AA).

The Level 1 analysis has been designed so that a factor of precision of 3 is necessary for detection of elements at their levels of hazard. In a recent comprehensive analysis of SSMS analysis of fly ash, it was found that, out of the 36 elements present at significant levels, 30 were determined with a factor of precision of less than 3.8. The problem elements for SSMS were notably beryllium, tellurium, gallium, cobalt, manganese and scandium. Work is currently in progress to improve sample preparation and analytical conditions for these elements.

In Level 1, SMSS is used to analyze solid samples for elements in solids, liquids, and SASS train particulate catches. Also, the XAD-2 organic resin used for trapping organics in the SASS train is also analyzed by SSMS but only after the application of specified ashing techniques to eliminate the organic matrix. Under Level 1, all samples which exceed 50 percent combustible material are also ashed before SSMS analysis. Since SSMS doesn't detect mercury with sufficient sensitivity, all of the above samples are analyzed by atomic absorption spectrophotometry for mercury. Aqueous solutions are analyzed as they are, but solid samples including SASS train particulate samples must first be digested by aqua regia for mercury analysis. The second and third SASS train solutions are analyzed only for mercury, arsenic and antimony by atomic absorption.

Leachate samples from storage piles, process feed streams, by-products, etc. are analyzed by ion-chromatography to determine anions such as nitrate, nitrite, sulfate, sulfite, phosphate, chloride, fluoride and cyanide.

ORGANIC ANALYSIS

The Level 1 organic analysis is accomplished using three analytical techniques: liquid chromatography (LC), infrared spectrophotometry (IR)

and low resolution mass spectrometry (LRMS) in conjunction with quantitation steps.

The Level 1 samples for organic analysis can be divided into four general types: gases, liquids, solids and solid extracts such as extracts from SASS train particulate and SASS train XAD-2 sorbent and aqueous solution. The analysis of organic gases has been discussed earlier. Organic solids such as coal and XAD-2 sorbent are pulverized and extracted in a Soxhlet extractor with methylene chloride. Organic liquids are entered into the organic analysis procedure with no previous treatment. Aqueous solutions including the SASS condensate containing organics are extracted with methylene chloride at pH 2 and 12. The two different pH solutions are combined and analyzed for their elements, and the methylene chloride extract is entered into the organic analysis procedure.

It has been explained how the various Level 1 samples are available either as methylene chloride extracts or neat organic liquids. For most of the solutions, it is necessary to concentrate to a volume of about 10 ml. However, before concentration, the organics which could be lost by solvent evaporation must be quantitized by the total chromatographable organic (TCO) method. This is accomplished by means of low resolution gas chromatography with a flame ionization detector. The quantitation is carried out by integrating the total detector response over a range covering organic compounds which boil between 100 and 300°C. The concentration is performed with a Kuderna–Danish apparatus with a three-ball Snyder column for volumes less than 1 litre and with a rotary evaporator for larger volumes. After the concentration, another TCO is run and an IR spectra of the concentrate is taken. Also, at this point, the higher boiling organics are quantitized by gravimetric (GRAV) analysis. The weight is obtained after drying to a constant weight in a dessicator over silica gel or Drierite. After concentration of the sample, it will be separated into seven fractions, based on polarity, by liquid chromatography (LC). The LC is carried out with a silica gel column and the following solvent series:

Fraction	*Solvent*
1	Pentane
2	20% Methylene chloride in pentane
3	50% Methylene chloride in pentane
4	Methylene chloride
5	5% Methanol in methylene chloride
6	20% Methanol in methylene chloride
7	50% Methanol in methylene chloride

In order for the separation to work, it will be necessary to remove any methylene chloride and water. The methylene chloride is removed by repetitively evaporating the methylene chloride in the presence of a small amount of silica gel and adding cyclopentane. The water is removed by a layer of specially cleaned, anhydrous sodium sulfate on top of the column. The cyclopentane solution of the sample and silica gel are added to the LC column and the seven fractions are eluted by successive addition of the seven solvents shown above. The TCO and GRAV procedures are performed for each of the fractions along with IR spectra. If any fraction contains more than a specified quantity when referenced back to the source, then it must be subjected to low-resolution mass-spectrometric analysis to determine compound categories, sub-categories and, when possible, compound identification. Interpretation of the LRMS spectra is aided by knowledge of the LC fraction and the IR spectra. From the LRMS data is obtained the chemical classes and the quantitation for Level 1. Report sheets are provided in the Level 1 manual[2] to facilitate the procedure for deriving the quantitative data for Level 1. In order to illustrate the Level 1 organic analysis methodology, it will be useful to follow the derivation from the LC work sheet through the organic summary sheet. For this example, a stack sample from a coal preheater has been selected. Table I shows the LC report sheet for this sample. Since the TCO plus GRAV amount of the concentrated extract exceeds 15 mg, the LC separation procedure is carried out. This is an unusually dirty sample but serves to illustrate Level 1 quite effectively. The sample was taken with an EPA Method 5 train specially modified for collecting polynuclear aromatic material (POM) during a source assessment of a coke plant coal preheater. The TCO and GRAV, their sums and the concentration referred to the total sample are entered on the first line of Table I. The amounts of the TCO and GRAV taken for the LC are also entered. After the LC has been run, one for the TCO and one for the GRAV samples, a TCO and GRAV are taken for each of the seven fractions. The weight (in milligrams) found in each fraction of the two runs are entered along with totals found by multiplying by the aliquot factor. Finally, the total mg for each fraction and the concentration referred to the original sample are entered. At this point, the weight per cubic meter of sample for each LC fraction is known. Level 1 specifies the concentrations of different types of samples where, if that concentration is exceeded, then LRMS should be run on that sample. That concentration for source vapor samples is 0.5 mg/m^3 and since all seven fractions exceed this amount, LRMS must be run on all seven. In order to assist in LRMS interpretation, an IR spectra is also run on each fraction. An example of the infrared report sheet is shown in Table II. This table consists of three

Table I.

LC REPORT

SAMPLE: 2A INLET STACK SAMPLE

	TCO, mg	GRAV, mg	TOTAL, mg	CONCENTRATION mg/m^3
TOTAL SAMPLE	547	1035	1582	1234
TAKEN FOR LC	54.7	103.5	158	
RECOVERED	52.7	89.0	142	

	TCO, mg		GRAV, mg			
FRACTION	FOUND	TOTAL	FOUND	TOTAL	TOTAL , mg	CONCENTRATION mg/m^3
1	11.1	111	13	130	241	188
2	30.5	305	36	360	665	520
3	3.4	34	7.8	78	112	87
4	0.77	7.7	2.2	22	30	23
5	1.2	12	3.0	30	42	33
6	4.3	43	23	230	273	213
7	1.3	13	3.8	38	51	40

TABLE II

IR REPORT

SAMPLE 2A INLET, FRACTION 2

FREQUENCY, cm^{-1}	INTENSITY	ASSIGNMENT/COMMENTS
3050	m	UNSATURATED CH STRETCH
2960, 2930, 2855	s	SATURATED CH_2, CH_3 STRETCH
2735	w	
1700	w	
1670	w	C = C OF ALKENE
1600	m	C = C AROMATIC RING STRETCHING/BROAD
1450, 1375	m	CH_2, CH_3 BEND
1300	w	
1260	w	
1190	w	C-H IN-PLANE BEND OF AROMATIC OR FUSED RING COMPOUNDS
1180, 1070	w	
1030	m	
960	w	
875	m	C-H OUT-OF-PLANE BEND OF AROMATIC OR FUSED RING COMPOUNDS
805	s	
745	s	

columns: frequency, intensity (strong, medium or weak) and assignment for each peak observed in the spectra. This spectra is for fraction 2 of the scrubber inlet. The spectra indicates the presence of alkanes, alkenes, aromatic rings and fused aromatic rings. These assignments are in agreement with the types of compounds expected for fraction 2, which should elute slightly polar compounds, such as aromatics.

TABLE III

LRMS REPORT

SAMPLE: 2 INLET FRACTION 2

MAJOR CATEGORIES

INTENSITY	CATEGORY	MW RANGE
100	FUSED ALTERNATE, NONALTERNATE HYDROCARBONS	<216
100	FUSED ALTERNATE, NONALTERNATE HYDROCARBONS	>216

SUB-CATEGORIES, SPECIFIC COMPOUNDS

INTENSITY	CATEGORY	m/e	COMPOSITION
100	NAPHTHALENE	128	$C_{10}H_8$
100	ALKYL NAPHTHALENES	142-156	$C_{11}H_{10}$-$C_{12}H_{12}$
100	ANTHRACENE/PHENANTHRENE	178	$C_{14}H_{10}$
100	ALKYL ANTHRACENE/PHENANTHRENE	192-290	$C_{15}H_{12}$-$C_{22}H_{26}$
100	ALKYL BIPHENYL	196-224	$C_{15}H_{16}$-$C_{17}H_{20}$
100	METHYL FLUORENE	180	$C_{14}H_{12}$
100	ALKYL PYRENE/FLUORANTHENE	216-272	$C_{17}H_{12}$-$C_{21}H_{20}$
10	BIPHENYLENE	152	$C_{12}H_8$

OTHER

10	EACH: OTHER ALKYLATED POLYCYCLICS, m/e 216 TO >300

The LRMS spectra interpretation (Table III) is aided by information already obtained from the LC fractionation and the IR spectra. The first level of information specifies the categories of compounds present. The next level of information identifies sub-categories. These categories and sub-categories coincide with a list of chemical species hazard levels known as the MEG (multimedia environmental goals) concentration.[3] Another level of information often available from LRMS is actual compound identification. These are listed on the report, if available. For each entry, an intensity is listed (100, 10, or 1, respectively) for major, minor, or trace components.

TABLE IV

ORGANIC EXTRACT SUMMARY TABLE

	SAMPLE: 2A INLET, STACK SAMPLE							
	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
TOTAL ORGANICS, mg/m^3	188	520	87	23	33	213	40	1100
TCO, mg	111	305	34	7.7	12	43	13	530
GRAV, mg	130	360	78	22	30	230	38	890
CATEGORY	mg/m^3							
ALIPHATIC HYDROCARBONS	10/188							188
AROMATICS		100/173						173
FUSED AROMATICS, <216 m/e		100/173	100/73	100/5.6	10/ 2.4			254
FUSED AROMATICS, >216 m/e		100/173	10/ 7.3	100/5.6	10/ 2.4			188
HETEROCYCLIC N COMPOUNDS				100/5.6	10/ 2.4	10/ 9.7	10/ 1.9	20
ESTERS				100/5.6	100/24	100/97	100/19	146
PHENOLS						100/97	100/19	116
UNCLASSIFIED			10/ 7.3	10/0.6	10/ 2.4	10/ 9.7	1/ 0.2	20

Finally, the data generated by the LC fractionation, the IR spectra, the TCO, the GRAV and the LRMS are brought together on the organic summary, Table IV, to obtain an estimate of the amount of material present in each of the MEG categories. The total organics concentration is referenced to the original sample for each LC fraction and are transferred from the last column of the LC report sheet. Each of the MEG categories found in the LRMS spectra is entered on a row in the bottom section of the table with the multiplying factor entered in the column for the fraction where it was found. The amounts from the total organics row are then distributed among the categories in proportion to the multiplying factors and entered in the boxes separated from the factors by slashes. Finally, the rows are summed to obtain the total concentration for each MEG category in the original sample. The concentrations in each category are carried on to Table V to compare the inlet and outlet to the DMEG

Table V

HAZARD LEVELS FOR STACK SAMPLES

COMPOUND CATEGORIES	TOTAL ORGANICS, mg/m³ 2A INLET	2A OUTLET	DMEG	HAZARD LEVEL 2A INLET	2A OUTLET
ALIPHATIC HYDROCARBONS	190	74	30.0	6.3	2.5
AROMATIC HYDROCARBONS	173	24	1.0	174.0	24.0
FUSED AROMATICS, <m/e 216	254	8	1.6	156.0	5.0
FUSED AROMATICS, >m/e 216	188	48	0.00002	9,400,000.0	2,400,000.0
HETEROCYCLIC N COMPOUNDS	20	33	0.1	200.0	330.0
ALCOHOLS, PHENOLS	120	–	2.0	60.0	–
ESTERS	150	31	0.12	1,250.0	250.0

(Discharge Multimedia Environmental Goal; i.e., a concentration of the substance estimated to cause minimum adverse effect on a healthy receptor) values. In order to express the hazard severity, the concentrations are divided by the DMEG values and presented as the discharge severity levels. It should be noted that the coal reheating process is very dirty and the hazard levels are all greater than one for the scrubber outlet as well as the inlet. The aliphatics category is the least hazardous component represented in the source. The DMEG for each category is that of the most hazardous compound in the category. In the case of the aliphatic category, the most hazardous compound in the category is dicyclopentadiene with a DMEG value of 30 mg/m^3, while the most hazardous compound in the category of fused aromatics of molecular weight > 216 is benzo(a)pyrene with a hazard level of 0.00002 mg/m^3. In

evaluating Level 1 data, it is necessary to assume that the most hazardous compound in the category is present unless there is analytical proof that a particular compound is not present. If it is proven not to be present, then the next most hazardous compound is assumed to be present and so on.

COMPARISON OF LEVEL 1 and 2 DATA

The phased approach to environmental assessment has been developed to enable the most economical yet comprehensive use of the analytical tools available in the current state of the art. The question has been asked: "How efficiently can Level 1 evaluate every aspect of a potential environmental hazard?" This question is still being asked and answered every time a source assessment is proposed and executed. So far, indications are that Level 1, when executed properly, is capable of safely characterizing the source and its potential hazards. Of course Level 1 may not provide the detail of more specialized and more costly techniques but, by raising the alarm that hazards from a given category are present, it can make their characterization much easier just because it has narrowed down the area of the search and all available resources to be concentrated on that area. Also, if Level 1 doesn't indicate that compounds from a particular category are present, then the investigation can safely be terminated with a minimum expenditure of resources.

To demonstrate how Level 1 works, data from the coal preheater will be compared to the Level 2 technique of gas chromatography mass spectrometry (GCMS).

For the first comparison (Table VI) the LC fractions 2, 3 and 4 were combined because the LC, IR and LRMS data showed that the three LC fractions were chemically similar. The first category is the MEG category of fused aromatics of molecular weight less than 216. The Level 1 LRMS data indicated the presence of seven sub-categories. Each of those sub-categories was verified by the Level 2/GCMS method. The Level 1 data gave a total of 254 mg/m^3 for the total category. The GCMS gave a total of 93 mg/m^3 and the individual concentrations contributed by 16 compounds or their analogs.

The second Level 1 and 2 comparison is for the MEG category of fused aromatics of molecular weight greater than 216 (Table VIII). The Level 1 data gave four sub-categories with a total of 188 mg/m^3 for the category. The Level 2 data showed several compounds or their structural isomers and their individual concentration contributions with a category total of 16 mg/m^3. This category contains the top level health hazard, benzo(a)pyrene, which has a DMEG value of 2×10^{-5} mg/m^3. The GCMS data gave a concentration for this compound of 0.14 on the scrubber inlet

and 0.01 on the outlet for discharge severities of 7000 and 500, respectively.

The third Level 1 and 2 comparison involves the combined LC fractions 5, 6 and 7 for the MEG category aromatics (Table VIII). The only Level 1 sub-category found was alkyl biphenyls for a category total concentration of 713 mg/m^3. The GCMS data gave seven compounds or their structural isomers, all or at least six coming under the Level 1/MEG sub-category of alkyl biphenyls. The GCMS total concentration was 49 mg/m^3.

Table VI.

LEVEL 1 AND 2 DATA COMPARISON FOR LC FRACTIONS 2, 3, AND 4 OF COAL PREHEATER INLET SAMPLE (DATA IN mg/m^3)

LEVEL 1 LRMS DATA		LEVEL 2 GCMS DATA	
MEG NO. 21, 22 CATEGORY: FUSED ABOMATICS mw < 216		COMPOUND	
NAPHTHALENE		NAPHTHALENE	10.13
ALKYL NAPHTHALENES		METHYL NAPHTHALENES	9.99
		DIMETHYL NAPHTHALENES	11.84
		TRIMETHYL	8.70
		TETRAMETHYL	5.15
METHYL FLUORENE		FLUORENE	1.13
		METHYL FLUORENE	1.70
		DIMETHYL FLUORENE	0.91
		METHOXY FLUORENE	21.29
ANTHRACENE/PHENANTHRENE		ANTHRACENE/PHENANTRENE	6.39
ALKYL ANTHRACENE/PHENANTHRENE		METHYL/PHENANTRENE	6.83
		DIMETHYL/PHENANTRENE	4.68
		PHENYL/PHENANTRENE	1.88
ALKYL PYRENE/FLUORANTHENE		FLUORANTHENE	0.59
ALKYL PYRENE/FLUORANTHENE		PYRENE	0.51
		METHYL PYRENES	1.66
TOTAL – 254		TOTAL –	93.29

The fourth comparison (Table VIII) was for MEG category heterocyclic nitrogen compounds. The only class indicated for Level 1 and GC/MS was carbazoles with concentrations of 5.6 and 3.68, respectively, for very close agreement.

The last comparison is for the MEG category phenols (Table IX). The sub-categories, phenols, alkylphenols and naphthols, were found in Level 1 with a category total of 116 mg/m^3. The GCMS data yielded eleven compounds or their structural isomers, all of which fall under the three Level 1 sub-categories. The GCMS category total was 18 mg/m^3.

Table VII.

LEVEL 1 AND 2 DATA COMPARISON FOR LC FRACTIONS 2, 3, AND 4 OF COAL PRE-HEATER INLET SAMPLE (DATA IN mg/m^3)

LEVEL 1 LRMS DATA	LEVEL 2 GCMS DATA	
MEG NO. 21, 22 CATEGORY: FUSED AROMATICS mw > 216	COMPOUND	
ALKYL ANTHRACENE/PHENANTHRENE	TRIMETHYL ANTHRACENES 220	2.28
ALKYL PYRENES/FLUORANTHENES	TETRAMETHYL ANTHRACENES	0.50
	METHYL PHENYL NAPHTHALENE	2.30
	BENZ(a)ANTHRACENE	0.39
	CHRYSENE/TRIPHENYLENE	0.79
	METHYL BENZANTHRACENE	1.22
	DIMETHYL BENZANTHRACENE	1.02
	BINAPHTHYL	0.9
FLUORANTHENES	BENZOFLUORANTHENES	0.42
	BENZO(E)PYRENE	0.36
	BENZO(A)PYRENE	0.14
ALKYL PYRENES	METHYL BENZO PYRENES	0.77
	INDENO (1,2,3-cd) PYRENE	0.02
	BENZO (g,h,i) PERYLENE	0.06
	DIBENZANTHRACENES	0.02
	3-METHYL CHOLANTHRENE	0.03
	DIMETHYL PHENYL NAPHTHALENE	5.62
TOTAL – 188.0	TOTAL –	16.84

Table VIII.

LEVEL 1 AND 2 DATA COMPARISON FOR LC FRACTIONS 5, 6, AND 7 OF COAL PRE-HEATER INLET SAMPLE (DATA IN mg/m^3)

LEVEL 1 LRMS DATA	LEVEL 2 GCMS DATA	
MEG NO. 15 CATEGORY: AROMATICS	COMPOUND	
ALKYL BIPHENYL	BIPHENYL	8.66
	METHYL BIPHENYL	4.63
	DIMETHYL BIPHENYL	3.29
	TRIMETHYL BIPHENYL	21.29
	TETRAMETHYL BIPHENYL	0.42
	TEREPHENYL	6.43
	METHOXY BIPHENYL	5.15
TOTAL – 173	TOTAL –	49.87
MEG NO. 23 CATEGORY: HETEROCYCLIC NITROGEN	COMPOUND	
CARBAZOLE AND ALKYL CARBAZOLES	CARBAZOLE	3.68
TOTAL – 5.6	TOTAL –	3.68

Table IX.

LEVEL 1 AND 2 DATA COMPARISON FOR LC FRACTIONS 5, 6, AND 7 OF COAL PRE-HEATER INLET SAMPLE (DATA IN mg/m^3)

LEVEL 1 LRMS DATA	LEVEL 2 GCMS DATA	
MEG NO. 18, 19, 20 CATEGORY: PHENOLS	COMPOUND	
PHENOLS	PHENOL	4.8
ALKYL PHENOLS	O-CRESOL	1.52
	M AND P-CRESOLS	2.34
	C2 PHENOLS	1.99
	C3 PHENOLS	0.82
	PHENYL PHENOLS	2.69
	METHYL PHENYL PHENOLS	1.76
	C2 PHENYL PHENOLS	0.70
NAPHTHOL SERIES	1-NAPHTHOL	TRACE
	2-NAPHTHOL	0.94
	METHYL NAPHTHOLS	0.82
TOTAL – 116	TOTAL –	18.3

Examination of the Level 1 and GCMS data just presented reveals that Level 1 was effective in flagging the presence of the MEG categories which include the hazardous compounds found by GCMS and that in all cases Level 1 tended toward a higher representation of the categories than GCMS. In general, these findings have been true in other cases where Levels 1 and 2 data have been compared. Reasons for greater category totals for Level 1 than for Level 2 could be that the GCMS method did not scan for mass units as high as those accounted for in Level 1, and the GCMS GC-columns have trouble in passing higher boiling, higher molecular weight compounds which are readily detected by the probe inlet technique used in LRMS. Also, it should be considered that Level 1 tends to be conservative by putting the full burden of the total LC fraction concentration for an occupied category on the compound with the lowest DMEG value in the category.

CONCLUSIONS

The phased approach to environmental assessment has been discussed and compared to the direct approach. It has been seen that the phased approach can be on the order 75 to 50 percent of the cost of the direct approach. The phased approach is effective and advantageous in narrowing down the area of investigation so that analytical resources can be concentrated on problem areas defined early in the phased approach. It

has been seen that the survey phase, Level 1, is efficient in flagging the compound categories for hazardous compounds in environmental samples.

The Level 1 sampling techniques cover the sampling and analysis of pollution sources with rigidly defined procedures aimed at isolation of samples sufficiently large for complete physical, chemical and biological characterization of environmental samples.

Level 2 sampling and analysis utilizes more quantitative techniques which are better able to determine the compound species harmful to the environment. The Level 2 techniques are applied after the Level 1 survey has directed the attention of the investigation to the MEG category that represents a threat to the environment. Since the scope of the investigation has been narrowed down, the analyst can exercise more discretion in the choice of analytical tools most suited to an effective identification of the problem species.

After Level 1 and Level 2 have identified problem species in a source, then Level 3 techniques may be employed to produce a complete profile of the problem—a function of system, process, weather, time and other variables.

References

1. J. W. Adams, K. T. Menzies and P. L. Levins. *Selection and Evaluation of Sorbent Resins for Collection of Organic Compounds.* EPA-600/7-77-044, (NTIS PB 268559), April 1977.
2. D. E. Lentzen, D. E. Wagner, E. D. Estes and W. Gutknect. *IERL-RTP Procedures Manual: Level 1 Environmental Assessment* (Second edition). EPA-600/7-78-201, (NTIS PB 293795), Research Triangle Park, NC October 1978.
3. J. G. Cleland and G. L. Kingsbury, Multimedia Environmental Goals for Environmental Assessment. Volumes I–IV. EPA-600/7-77-136a and b, (NTIS PB 276919 and 276 920), November 1977. EPA-600/7-79-176a and b, (NTIS PB 80-115108 and 80-115116), August 1979, Research Triangle Park, NC.